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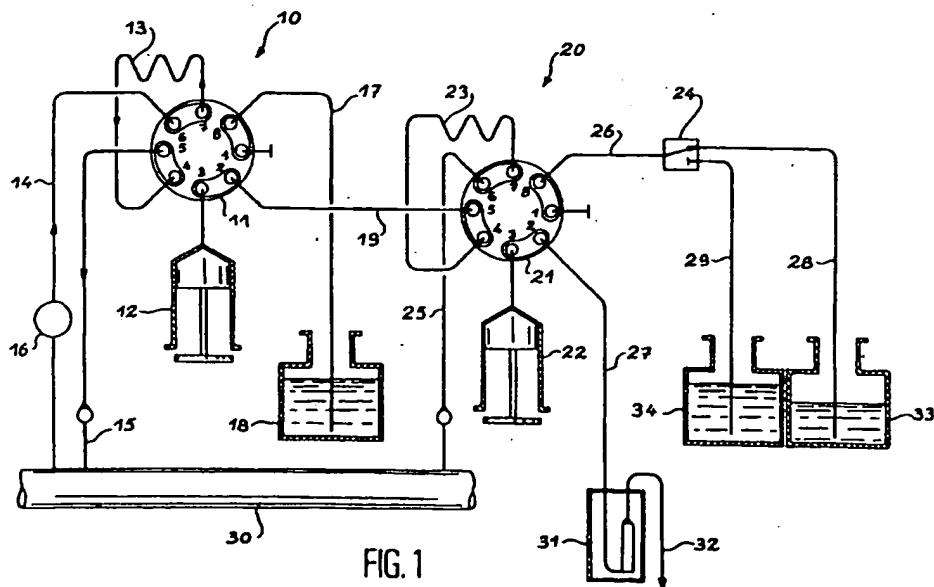
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## (54) Automatic sampling, diluting and analysing module

(57) The module has first and second sections 10, 20 containing eightway valves 11 and 21 which are operable to sample test liquid 30, add diluents 18 and 33 and reagent 34 prior to analysis 31. Typically the first section samples the test liquid using a pump 16 to supply a loop 13. Syringe 12 sucks up diluent 18 and then scavenges liquid from the loop for dilution and supply to a second loop 23. Another syringe 22 scavenges the now diluted sample from the second loop 23 and sucks up reagent 34 and diluent 33 and then delivers the resulting sample/reagent/diluent mixture to an analyser 31. Utility is in analysing hydrazine in solutions used in nuclear fuel reprocessing using dimethylaminobenzaldehyde reagent.



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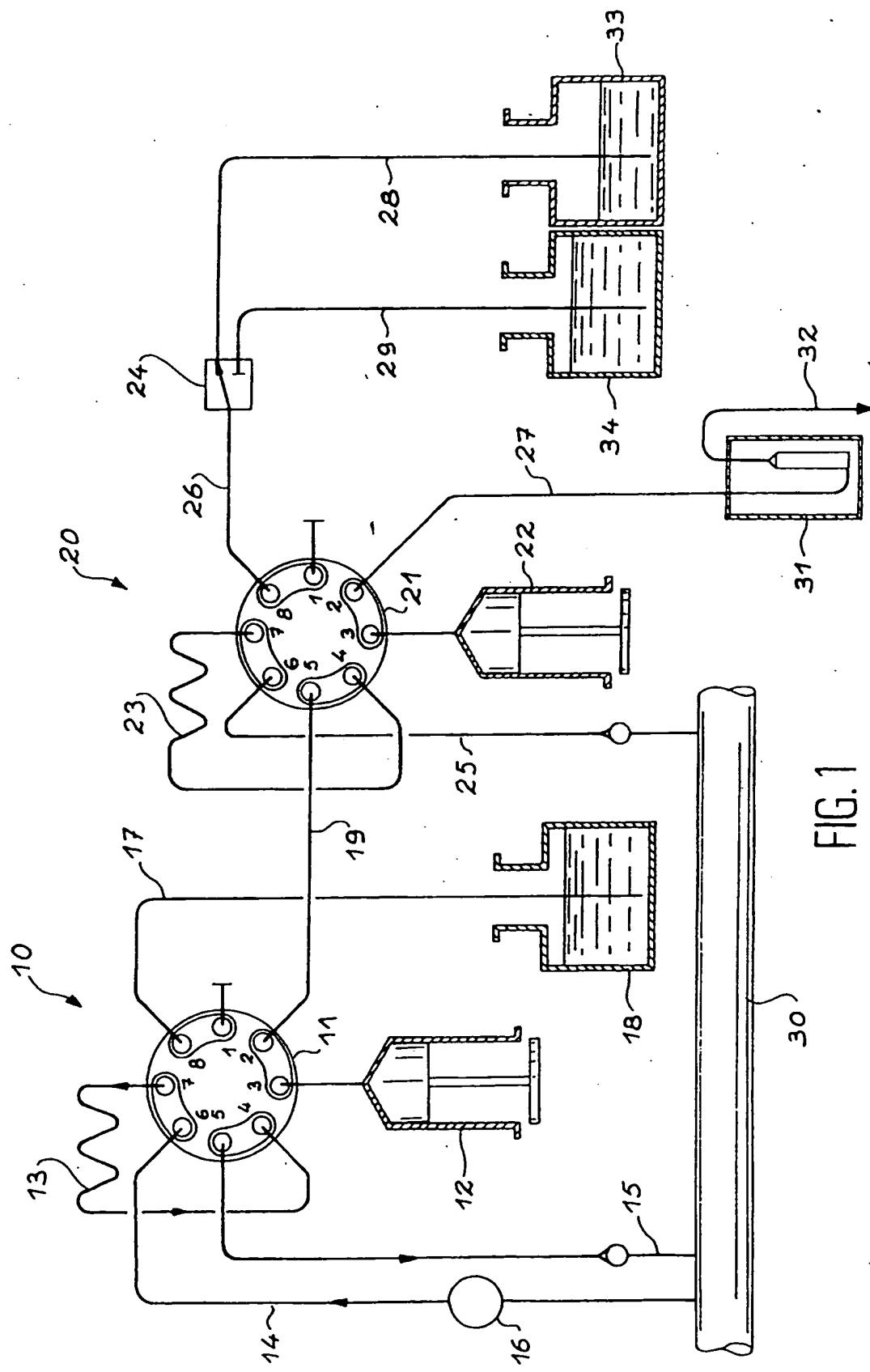


FIG. 1

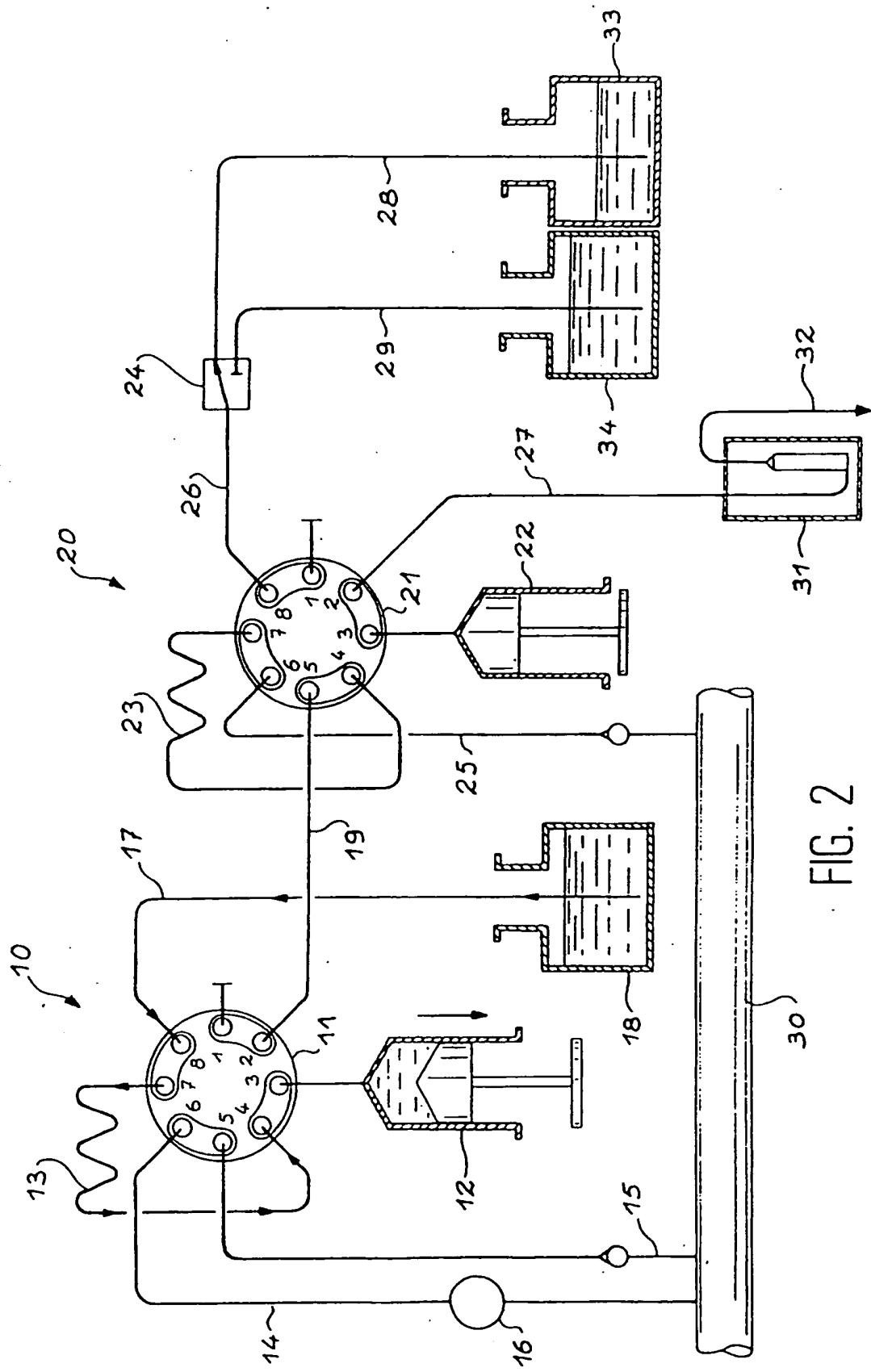
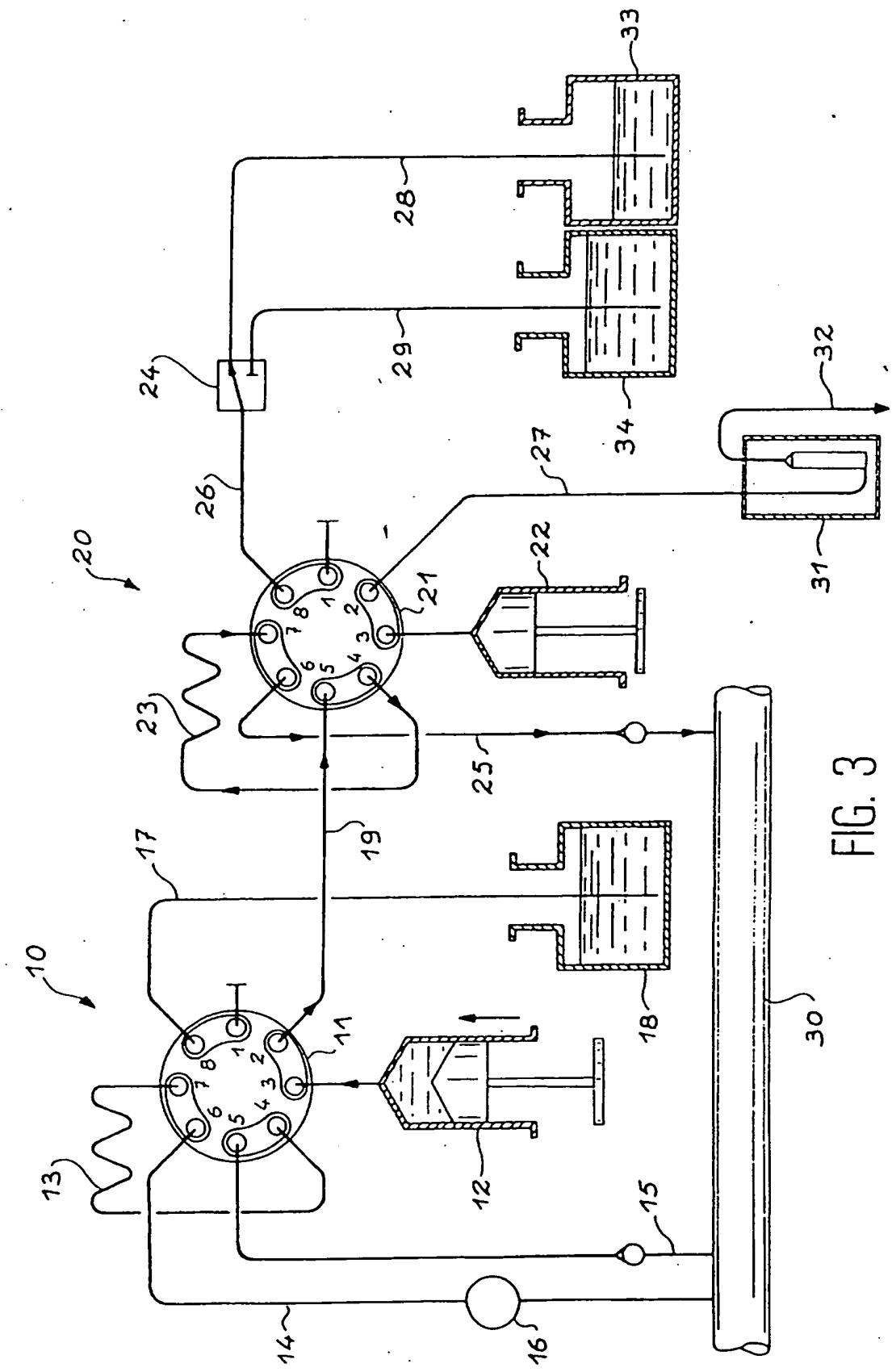


FIG. 2



4/6

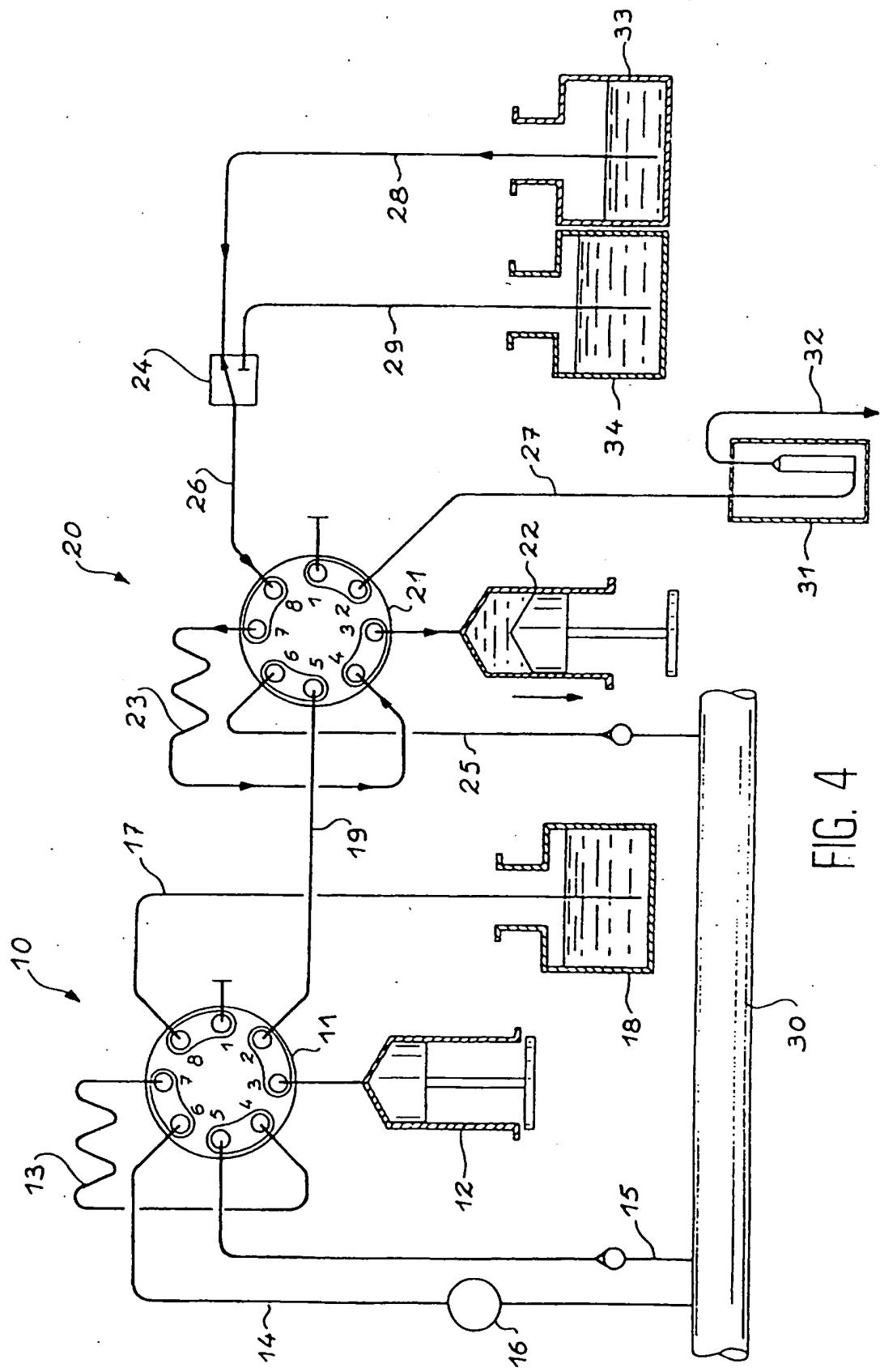
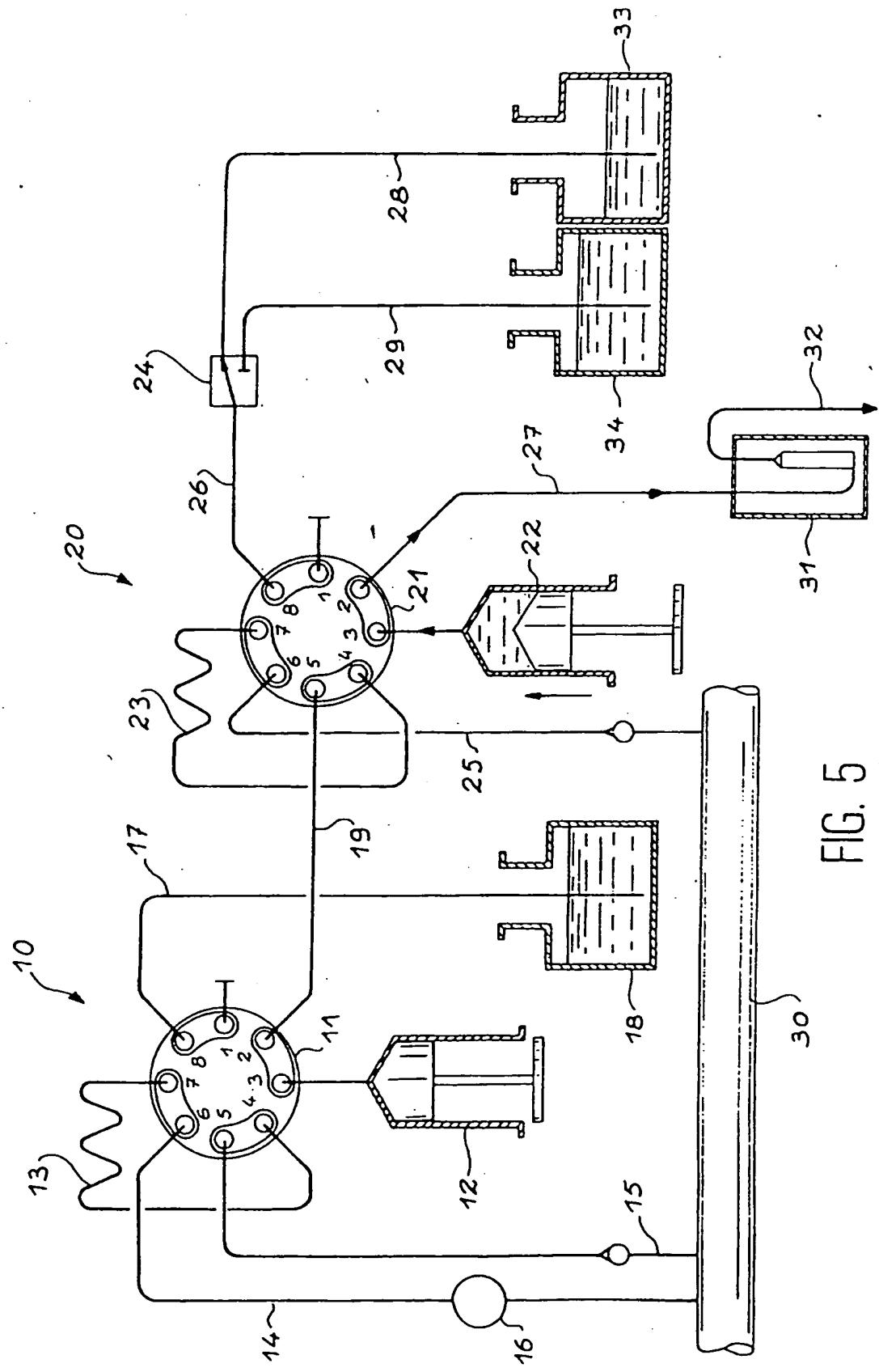
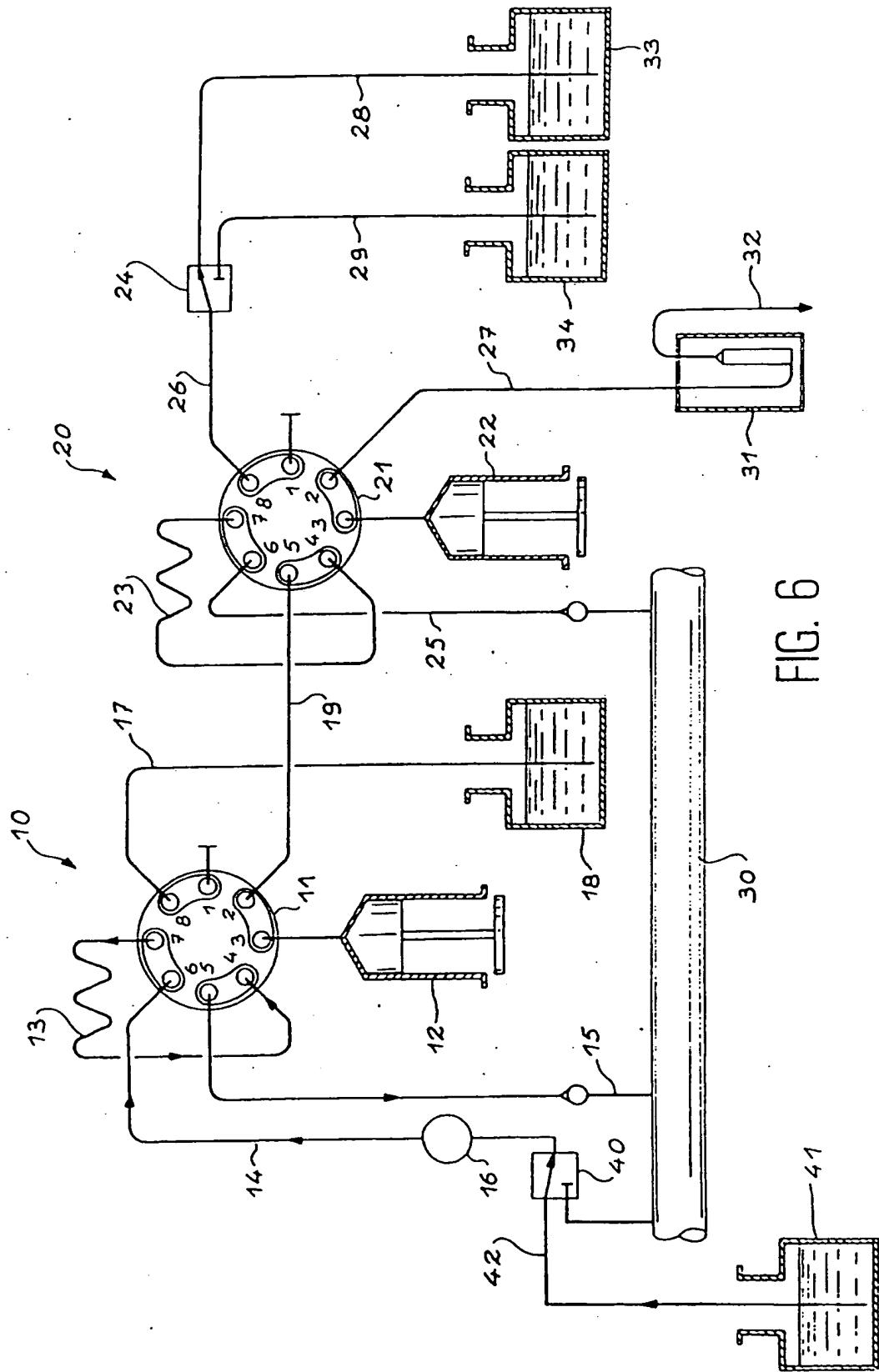


FIG. 4

5/6



6/6



FLUIDIC MODULE FOR AUTOMATIC ANALYSIS DEVICE

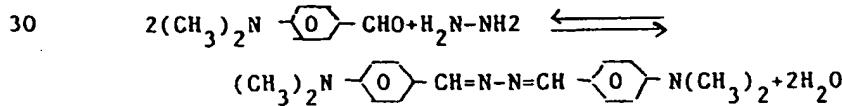
The invention relates to a fluidic module for an automatic analysis device. It is more particularly used in the determination of the hydrazine concentration in a solution used in nuclear fuel reprocessing processes.

Hydrazine is a compound used as a stabilizer in nuclear fuel reprocessing processes. The hydrazine concentration of a solution, in certain stages of the reprocessing, constitutes an important parameter, both for the performance of the reprocessing process and for the safety of the installation. This parameter is determined by spectrophotometric analysis in the laboratory on samples taken during the performance of the process. Analysis takes place at variable time intervals after sampling, which is prejudicial to the reproducibility of the measurements. Thus, the reactions with the hydrazine are continued in the sample following sampling. Moreover, the sampled quantity is not minimized, which needlessly increases the volume of active analytical effluents.

The hydrazine concentration can be measured by Raman spectrophotometry. However, this method lacks sensitivity.

Another interesting method is ion chromatography, which also gives access to the hydroxylamine on the same sample. However, the chromatography column regeneration time makes this method difficult to automate.

It is possible to determine the hydrazine concentration of a solution by the so-called DMAB (dimethylaminobenzaldehyde) method. The reaction taking place in this method is as follows:



The hydrazone obtained, which is a very conjugate molecule, has an absorption peak at 455 nm with a high molar extinction coefficient (approximately 60,000). Thus, this reaction is very equilibrated. Rapid measurements on the value of K:

$$K = \frac{[\text{hydrazone}]}{(\text{DMAB})^2 [\text{hydrazine}]}$$

have demonstrated that it is around  $7.10^{-3}$ . This makes it necessary to work with a very large aldehyde excess in order to make the free hydrazine quantity negligible. The ratio between the DMAB concentration and the hydrazine concentration for the automatic analysis has been fixed at around 15,000.

- 5 As the hydrazine concentration in the solution to be tested is approximately 0.2 M, this imposes a total dilution of 10,000 in order to have measurable optical densities. It has also been found that the temperature greatly influences the optical density value. It is probable that the constant K varies with the temperature. This makes it possible to keep at a constant  
10 temperature the system formed by the apparatus and the reagents.

What the inventors of the present invention have attempted to obtain in the particular case of hydrazine is a device generating very little in the way of analytical effluents and having a very short response time of 2 to 3  
15 minutes between the sampling instant and the result of the analysis, which does not enable the hydrazine to have sufficient time to react so as to falsify the result.

They have designed a sequential analytical device using the DMAB method,  
20 which is able to supply in a short time of 2 to 3 minutes the hydrazine concentration of the solution with a precision of 1 to 2% and with quasi-negligible analytical effluents (1 to 2  $\mu$ l of the total sample).

Thus, the invention relates to a fluidic module for an automatic analysis  
25 device making it possible to determine the concentration of a substance in a solution, incorporating means for sampling a fraction of the solution, means for contacting the sampled solution with a reagent so that the substance contained in the sampled solution reacts with the reagent, means for supplying the sampled solution fraction which has reacted with the reagent to an  
30 apparatus for measuring the absorbance of the product obtained during the reaction in order to deduce therefrom the concentration of the substance in the solution, characterized in that:

- the fluidic module comprises a first member making it possible to sample a given quantity of solution and add to it a given quantity of dilution  
35 product in order to obtain a first dilution of the solution,
- the fluidic module also comprises a second member making it possible to

sample a fraction of the solution diluted by the first member, to add to it a given reagent quantity and a given dilution product quantity so as to obtain a second dilution and then supply the resulting solution to the measuring apparatus,

- 5 - the first member comprises a first, two-position, eight-way valve, whereof two ways are connected to a first and to a second pipe of a solution sampling circuit, two ways are connected to first means for the storage of a given liquid quantity, one way is connected to a pipe for supplying the dilution product, one way is connected to a first pump, one way, called the 10 outlet way, is connected to the second member, one way is sealed and the connections taking place in such a way that:

\*in the first position of the first valve, the first storage means are connected to the sampling circuit, the dilution product supply pipe is connected to the sealed way and the outlet way is connected to the first 15 pump,

- \*in the second position of the first valve, the first storage means are connected to the first pump on the one hand and to the dilution product supply pipe on the other, the pipes of the sampling circuit being directly interconnected and the outlet way is connected to the sealed way,  
20 - the second member comprises a second, two-position, eight way valve, whereof two ways are connected to second means for storing a given liquid quantity, one way, called the inlet way, is connected to the outlet way of the first valve, one way is connected to a delivery pipe, one way is sealed, one way is connected to the outlet way of a third valve having two inlet 25 ways, whereof one is connected to a reagent supply pipe and the other to a dilution product supply pipe, one way is connected to a second pump, one way is connected to a pipe directing the resulting solution to the measuring apparatus, the connections being made in such a way that:

\*in the first position of the second valve, the second storage means are 30 connected on the one hand to the inlet way of the second valve and on the other to the delivery pipe, the outlet way of the third valve is connected to the sealed way of the second valve and the second pump is connected to the pipe directing the resulting solution to the measuring apparatus,

\*in the second position of the second valve, the sec nd storage means are 35 connected on the one hand t the second pump and on the other to the outlet way f the third valve, the inlet way of the second valve is c nnected to

the delivery pipe and the sealed way of the second valve is connected to the pipe directing the resulting solution to the measuring apparatus.

The storage means of each member can be constituted by a loop and the pump 5 can be a syringe.

The substance whose concentration is to be determined can e.g. be a chemical compound or a simple substance or element.

10 The invention is described in greater detail hereinafter relative to a non-limitative embodiment of the automatic analysis of hydrazine in a solution used in nuclear fuel reprocessing processes, accompanied by the attached drawings, wherein show:

15 Figs. 1 to 5 A fluidic module for an automatic analysis device according to the invention, at different stages of its operation.

Fig. 6 The fluidic module of the preceding drawings supplemented with a view to the calibration of the automatic analysis 20 device.

The apparatus shown in figs. 1 to 5 comprises a first member 10 formed by a two-position, eight-way valve 11, a syringe 12 and a loop 13 produced from a tube and which can contain a given liquid quantity. This apparatus also 25 comprises a second member 20 formed by a two-position, eight-way valve 21, a syringe 22, a loop 23 (formed in the same way as the loop 13) and a valve 24.

Thus, the valves 11 and 21 have eight ways numbered 1 to 8. A first position 30 makes it possible to simultaneously connect way 2 to way 3, way 4 to way 5, way 6 to way 7, way 8 to way 1 for each valve. A second position makes it possible to simultaneously connect way 1 to way 2, way 3 to way 4, way 5 to way 6, way 7 to way 8 for each valve.

35 For each valve 11 and 21, the way 1 is sealed, the loop 13 or 23 is connected between the ways 4 and 7 and the syringe 12 or 22 is connected to way 3.

The pipe 30 in which circulates the solution to be analyzed, is connected to the valve 11 by a branch circuit constituted by a pipe 14 for supplying the sampled solution and a return pipe 15. A pump 16 permits the circulation of the solution in the branch circuit.

5

A pipe 17 connects way 8 of valve 11 to a tank 18 containing an appropriate diluent, such as nitric acid. A pipe 19 connects way 2 of valve 11 to way 5 of valve 21.

10 For valve 21, a delivery pipe 25 connects way 6 to pipe 30, a pipe 26 connects way 8 to the outlet way of valve 24, a pipe 27 connects way 2 to the hydrazone absorbance measuring apparatus 31 and a pipe 32 makes it possible to discharge the analyzed liquid.

15 The valve 24 has a first inlet way connected by a pipe 28 to a tank 33 containing an appropriate diluent, such as nitric acid. The second inlet way of valve 24 is connected by a pipe 29 to a tank 34 containing DMAB.

For example, the capacity of the loops 13 and 23 can be 0.1 ml and that of  
20 the syringes 12 and 22 10 ml.

The operation of the device will now be described relative to figs. 1 to 5. On starting up analysis, the valves 11 and 21 are in the position indicated in fig. 1, i.e. in their first position. The syringes 12 and 22 are empty,  
25 their piston being pushed to the bottom. The pump 16 brings about a circulation of the fluid to be analyzed through the loop 13. When the content of the loop 13 is considered to be representative of the solution to be analyzed, the pump 16 is stopped and the valve 11 passes into its second position, as indicated in fig. 2. The syringe 12 is then put into operation.  
30 It sucks up the diluent contained in the tank 18, whilst scavenging the loop 13. Experience has shown that at the end of the filling of the syringe 12, the sucked solution is quasi-homogeneous. A limited amplitude reciprocating movement on the piston of the syringe 12 makes it possible to complete the uniformity of the sucked solution.

35

The valve 11 then returns to its first position, as shown in fig. 3. The

syringe 12 expels its content by way 5 of valve 21 to the loop 23, returning to the pipe 30 by way 6 of valve 21, all said first dilution, with the exception of the content of loop 23.

- 5 The valve 21 then passes into its second position, as shown in fig. 4. The syringe 22 is then started up. It firstly sucks up the reagent DMAB contained in the tank 34, whilst scavenging the loop 23. By switching the valve 24, it then sucks up the diluent contained in the tank 33. The homogeneity or uniformity of the drawn off mixture is obtained as indicated  
10 hereinbefore by a small amplitude reciprocating movement.

The valve 21 then returns to its first position, as shown in fig. 5. The syringe 22 then discharges its content through the cell of the measuring apparatus 31. The measurement takes place a few instants after the end of  
15 the movement of the syringe 22.

A description will now be given of the calibration cycle of the automatic analysis device. Knowing that the Lambert Beer law is respected in the measuring range, calibration takes place in two stages, namely the blank  
20 reagent and measurement of the standard.

For calibration on the basis of the blank reagent, the valve 21 is in its second position and pure diluent is introduced into the loop 23. The syringe 22 sucks up the reagent contained in the tank 34 and then the diluent contained in the tank 33, selection taking place by means of the valve 24. The valve 21 then returns to its first position and the syringe 22 delivers the blank reagent into the photometer cell. The photometric signal  
25 is acquired.

- 30 Calibration can be continued by having a standard solution in place of the sample. However, it is also possible to envisage an entirely automatic calibration programmed at regular intervals. Fig. 6 illustrates this solution. To the previously described fluidic module is added a valve 40, which enables the pump 16 to pump either the solution to be analyzed in the pipe  
35 30, or the content of a tank 41 by means of a pipe 42. Thus, the loop 13 can be filled with a standard solution with an equivalent concentration to

that of the solution to be analyzed, said standard solution filling the tank  
41. An advantage of this is that it is possible to completely test the  
entire measuring line.

5 The result of the sample concentration is given by the relation:

$$C_x = \frac{\log \frac{I_B}{I_x}}{\log \frac{I_B}{I_E}} \times C_{Et}$$

10 with  $C_x$  representing the sample concentration,  $I_B$  the photometric unprocessed signal of the blank reagent,  $I_E$  the photometric unprocessed signal of the standard,  $I_x$  the photometric unprocessed signal of the sample and  $C_{Et}$  the concentration of the standard.

Thus, it is possible to obtain an automatic hydrazine analysis device having  
a fluidic module according to the invention, most of which can be included  
20 in a glove box, but the photometer, a control module for the device and a  
printer for collecting the results can be located outside the box. The  
connection to the photometer can take place by means of optical fibres.  
The latter carry the light signals through the glove box and consequently  
the complete photometric assembly can be located outside the box.

25 The control module controls the complete device by means of a GESPACK card  
organized around the Motorola microprocessor 68000. The input/output cards  
can also be of a commercially available nature. The analog/digital conversion  
card can be of design SPRA/GSIA.

30 The limit positions of the syringes can be detected by switches. The limit  
positions of the dilution valves can be detected by measuring the current  
flowing in the valve drive motor. A sudden increase in the current is  
interpreted as a mechanical blockage and the motor supply is interrupted.

35 The results are edited on a printer and can be transmitted to a computer.

A device equipped with the fluidic module according to the invention has been tested and gives the following results:

- analysis time : 2 minutes,
- precision : 1 to 2% in the hydrazine range 0.1 to 0.3 M,
- 5 - sample volume effectively sampled on the pipe : 1  $\mu$ l per analysis,
- analytical effluent volume for each analysis : 1  $\mu$ l of sampled volume diluted in 10 ml of diluent.

CLAIMS

1. Fluid module for an automatic analysis device making it possible to determine the concentration of a substance in a solution, incorporating  
5 means for sampling a fraction of the solution, means for contacting the sampled solution with a reagent so that the substance contained in the sampled solution reacts with the reagent, means for supplying the sampled solution fraction which has reacted with the reagent to an apparatus (31) for measuring the absorbance of the product obtained during the reaction in  
10 order to deduce therefrom the concentration of the substance in the solution, characterized in that:

- the fluidic module comprises a first member (10) making it possible to sample a given quantity of solution and add to it a given quantity of dilution product in order to obtain a first dilution of the solution,
- 15 - the fluidic module also comprises a second member (20) making it possible to sample a fraction of the solution diluted by the first member, to add to it a given reagent quantity and a given dilution product quantity so as to obtain a second dilution and then supply the resulting solution to the measuring apparatus (31),
- 20 - the first member (10) comprises a first, two-position, eight-way valve (11), whereof two ways are connected to a first (14) and to a second (15) pipe of a solution sampling circuit, two ways are connected to first means (13) for the storage of a given liquid quantity, one way is connected to a pipe (17) for supplying the dilution product, one way is connected to a first pump (12), one way, called the outlet way, is connected to the second member (20), one way is sealed and the connections taking place in such a way that:

\*in the first position of the first valve (11), the first storage means (13) are connected to the sampling circuit, the dilution product supply pipe (17) is connected to the sealed way and the outlet way is connected to the first pump,

\*in the second position of the first valve, the first storage means (13) are connected to the first pump (12) on the one hand and to the dilution product supply pipe (17) on the other, the pipes (14, 15) of the sampling circuit being directly interconnected and the outlet way is connected to the sealed way,

- the second member (20) comprises a second, two-position, eight way valve (21), whereof two ways are connected to a second means (23) for storing a given liquid quantity, one way, called the inlet way, is connected to the outlet way of the first valve (11), one way is connected to a delivery pipe (25), one way is sealed, one way is connected to the outlet way of a third valve (24) having two inlet ways, whereof one is connected to a reagent supply pipe (29) and the other to a dilution product supply pipe (28), one way is connected to a second pump (22), one way is connected to a pipe (27) directing the resulting solution to the measuring apparatus (31), the  
5 connections being made in such a way that:

\*in the first position of the second valve (21), the second storage means (23) are connected on the one hand to the inlet way of the second valve (21) and on the other to the delivery pipe (25), the outlet way of the third valve (24) is connected to the sealed way of the second valve and the second  
15 pump is connected to the pipe directing the resulting solution to the measuring apparatus,

\*in the second position of the second valve (21), the second storage means are connected on the one hand to the second pump (22) and on the other to the outlet way of the third valve (24), the inlet way of the second valve (21) is connected to the delivery pipe (25) and the sealed way of the second valve (21) is connected to the pipe (27) directing the resulting solution to the measuring apparatus (31).

2. Fluidic module according to claim 1, characterized in that each of said  
25 storage means (13, 23) is in the form of a loop.

3. Fluidic module according to either of the claims 1 and 2, characterized in that each pump (12, 22) is constituted by a syringe-type device.

30 4. Fluidic module according to any one of the claims 1 to 3, characterized in that a valve (40) is provided on the solution sampling circuit permitting the sampling of either the solution to be analyzed or a standard solution.

5. Application of the fluidic module according to any one of the claims 1 to 4 to the determination of the hydrazine concentration in a solution, the reagent being dimethylaminobenzaldehyde (DMAB) and the product obtained being hydrazone.

6. Application of the fluidic module according to claim 5, characterized in that the solution containing the hydrazine to be analyzed is used in a nuclear fuel reprocessing process.

12

**Patents Act 1977**  
**Examiner's report to the Controller under Section 17**  
**(The Search report)**

<b>Relevant Technical Fields</b>		Application number GB 9522205.5
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(ii) Int Cl (Ed.6)      GO1N 1/20, 35/00		Date of completion of Search 15 JANUARY 1996
<b>Databases (see below)</b> (i) UK Patent Office collections of GB, EP, WO and US patent specifications.		Documents considered relevant following a search in respect of Claims :- 1-6
(ii) ONLINE: WPI, CLAIMS, JAPIO		

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